

Every Molecule Tells a Story



Simon Cotton

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Simon Cotton

Honorary Senior Lecturer in Chemistry
University of Birmingham, UK

Chemist Emeritus
Uppingham School, UK



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Dedication

The late Nikolaus Pevsner famously dedicated the Bedfordshire, Huntingdon, and Peterborough volume of his Buildings of England series to the “Inventor of the Iced Lolly.”

As a teacher without easy access to a university library, I have felt there could be something to be said for a dedication to the Internet, were it not for Sir Timothy Berners Lee and his invention, this book would not have been possible.

Instead, however, I dedicate this book to Hilary, to Jill, to Judith, and to Lisa, for their encouragement, assistance, and inspiration.

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Preface

Everything that exists is made of atoms, and most of those substances contain groups of two or more of these bonded together to form molecules. Chemistry is the science of molecules. From cooking to medicine, from engineering to art, it is everywhere.

What is this book? For a start, it is not a textbook, nor is it a collection of reviews. If I can put this into words, it is a celebration of molecules and of chemistry. Over 200 molecules that give you life, enrich your life, or may end your life if you are not careful. Though I cannot write as well or as clearly as Peter Atkins or John Emsley, I have tried to say why I think that these molecules matter, putting them into their context rather than seeing them as just substances of academic interest. I've possibly written more than I should have concerning some molecules that I have found interesting, topical, or concerning which it does not seem so easy to obtain information, but the reader will judge that. For many years, chemistry has been described as the central science, notably in America. Despite that, it has been an unfashionable area. I have been unfashionable for most of my life, so I am not worried about that. It is primarily addressed to chemistry students on either side of the school/university divide and to their teachers. I even nurse a vain hope that it might become something of a *vade mecum* to teachers and lecturers and, to this end, I have done my best to provide a fairly comprehensive bibliography.

This book has been over 3 years in the making, 2 years in the writing, and perhaps 18 years in its conception, when I picked up a copy of, I think, *Time* magazine in February 1993, read an article about chocolate and phenylethylamine, and decided that it would be a good vehicle to teach students about amine chemistry. That led to “Soundbite Molecules”, then to “Molecule of the Month”, and, eventually, to this book. But I can sympathise with the writer of Ecclesiastes 12:12 in his comment “of making many books there is no end; and much study is a weariness of the flesh”.

Many people have discussed or helped with material, including authors who have sent copies of papers. Among the individuals I should thank are, from the Chemistry Department of the University of Cambridge, Peter Wothers, Judith Battison, and Mike Todd-Jones for their help in different ways, and Phillip Broadwith and Nina Notman of the Royal Society of Chemistry for giving me the opportunity to write and deliver “Chemistry in Its Element—Compounds” podcasts on the Chemistry World site. Paul May of the University of Bristol has, over the past decade, not just tolerated my attempts to write “Molecule of the Month” for its website, but also given me material assistance in producing them. Successive members of the editorial team of the RSC’s *Education in Chemistry* have helped me on the way, especially Kathryn Roberts, who, in 1996, believed in my idea of “Soundbite Molecules” and gave it air time within the pages of the journal. Finally, I would particularly like to thank those who have most often advised, commented, answered queries, and procured pdf files for me—namely, James Anderson, Peter Bodily, John Emsley, Gordon Gribble, John Mann, and Geoff Rayner-Canham.

So here it is then, ladies and gentlemen; I hope that you find this book useful or even valuable, though I have come to share the view of Saint Thomas Aquinas that all I have written seems like so much straw.

Simon Cotton
Holy Saturday 2011

The Author

Simon Cotton obtained his BSc and PhD at Imperial College London, followed by research and teaching appointments at Queen Mary College, London, and the University of East Anglia. He subsequently taught chemistry in both state and independent schools for over 30 years, retiring from Uppingham School as Chemist Emeritus. In September 2011, he was appointed an Honorary Senior Lecturer in the Department of Chemistry at the University of Birmingham. He has lectured widely in the UK, and carries out research on the chemistry of iron, cobalt, scandium, and the lanthanide elements.

His “Soundbite Molecules” feature has run as a regular column in the magazine *Education in Chemistry* since 1996, reaching every secondary school in the UK. He has written nearly 40 “Molecules of the Month” columns, which are featured online at <http://www.chm.bris.ac.uk/motm/motm.htm> and recognised globally. Additionally, he has delivered over a dozen “Chemistry in Its Element” podcasts for the Royal Society of Chemistry’s *Chemistry World* website at <http://www.rsc.org/chemistryworld/>.

In 2005 he shared the Royal Society of Chemistry Schools Education Award. He was editor of “Lanthanide and Actinide Compounds” for the *Dictionary of Organometallic Compounds* and the *Dictionary of Inorganic Compounds* (Chapman and Hall) between 1984 and 1997.

He wrote the account of lanthanide coordination chemistry for the second edition of *Comprehensive Coordination Chemistry* (Pergamon) and the accounts of lanthanide inorganic and coordination chemistry for the first and second editions of the *Encyclopedia of Inorganic Chemistry* (Wiley).

This is his sixth book; his previous books are

- D. J. Cardin, S. A. Cotton, M. Green, and J. A. Labinger, *Organometallic Compounds of the Lanthanides, Actinides and Early Transition Metals*, London: Chapman & Hall, 1985.
- S. A. Cotton, *Chemistry of Precious Metals*, London: Blackie, 1997.
- S. A. Cotton, *Lanthanide and Actinide Chemistry*, Chichester, England: John Wiley & Sons, 2006.
- S. A. Cotton, *Lanthanides and Actinides*, Basingstoke, England: Macmillan, 1991.
- S. A. Cotton and F. A. Hart, *The Heavy Transition Elements*, Basingstoke, England: Macmillan, 1975.

1 Atmosphere and Water

NITROGEN (DINITROGEN, N₂)



Though nitrogen gas, first isolated in 1772 by the Scottish doctor Daniel Rutherford, makes up over three-quarters of the atmosphere (in dry air, 78.08% to be precise), it is so unreactive that people might question its value. The very strong triple bond in the nitrogen molecule (1.1) makes it very unreactive in a chemical laboratory, though one or two very hot metals like magnesium have enough energy to break the bond and combine. In contrast to the 450°C and 200 times atmospheric pressure needed for a reasonable yield in the Haber process, the nitrogenase enzyme in rhizobium bacteria, found in nodules on the roots of leguminous plants (e.g., pea, bean, vetch, clover, lentil, alfalfa, lupin, peanut) can “fix” nitrogen at ambient temperature and pressure. Some fixation also occurs in thunderstorms when nitrogen and oxygen react to form nitrogen oxides as a flash of lightning supplies the energy.

This lack of reactivity of N₂ is vital, however, because it dilutes the oxygen present in the atmosphere and ensures that forest fires and other combustion reactions do not get out of control. On January 27, 1967, three astronauts were killed as a fatal fire swept through the command module, mounted on a Saturn rocket, in a test run for the first Apollo mission at Cape Kennedy. The speed of the spreading fire was due to the use of a pure oxygen atmosphere in the cabin, and this was subsequently replaced by a 60% O₂ and 40% N₂ mixture. Humans function better breathing a nitrogen–oxygen mixture; pure oxygen leads to problems like fluid buildup in the lungs.

Large amounts of nitrogen are by-products of the manufacture of oxygen by fractional distillation of liquid air, and its chemical inertness finds particular application as an “inert atmosphere” in industry, car tyres, and fuel systems, as well as in packaged foods (e.g., potato crisps). Liquid N₂ (b.p. –196°C) is the most widely used cryogenic refrigerant. For many years it was believed that N₂ would not bind to a metal, unlike the O₂ molecule; however, since the isolation of [Ru(NH₃)₅(N₂)]²⁺ in 1965 by Allen and Senoff, many dinitrogen complexes have been isolated. It is accepted that a metal–N₂ complex is involved in the fixation of nitrogen by the molybdenum- and iron-containing enzyme nitrogenase, and chemists are still trying to find a way of carrying this out under mild conditions in industry.

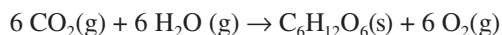
Even though it is much less abundant in the earth, the interchange of nitrogen between the atmosphere and living systems in the nitrogen cycle is vital because it is an essential element in all amino acids (and proteins); likewise, a wide range of nitrogen compounds have immense commercial importance, such as ammonia and nitric acid in making fertilisers, explosives, and dyestuffs (see pp. 38–39 and 119, 122). Nitrogen molecules are unreactive, yet conversely it is the immense strength of the

$\text{N}\equiv\text{N}$ bond (bond energy 945 kJ mol^{-1}) which contributes to the energy release from nitrogen-based explosives like TNT and ammonium nitrate in which N_2 is formed as a product.

OXYGEN (DIOXYGEN, O_2)



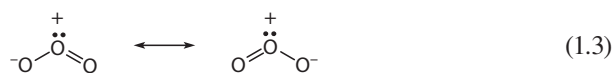
Oxygen is the most abundant element in the earth and the second most abundant in the atmosphere (21.0% by volume, in dry air). It is absolutely essential for life; living organisms depend upon it for cellular respiration, and it owes its presence in the air to photosynthesis in green plants, in the simplified form:



The discovery and isolation of O_2 gas by Priestley and Scheele in 1773–1774 and its subsequent exploitation in the understanding of combustion by Lavoisier were a key step in the development of chemistry. Along with nitrogen, oxygen is produced industrially in excess of 100 million tons a year by the fractional distillation of liquid air, the separation relying upon the difference in the boiling points of nitrogen (77K; -196°C) and oxygen (90K; -183°C). Liquid nitrogen and liquid oxygen also differ in their colours: colourless and pale blue respectively. Industrially, oxygen is used in large quantities to make steel and other chemicals, to support combustion and generation of high temperature (e.g., H_2/O_2 rockets, oxy-acetylene cutters), and in life support in health care (oxygen tents and masks, emphysema treatment, divers, aircraft, and spaceflight). Oxygen has a small but significant solubility in water that is essential to marine and aquatic life; its solubility decreases with increasing temperature, so a tropical fish tank requires an aerator.

The oxygen molecule (1.2) contains a strong $\text{O}=\text{O}$ bond (bond energy 498 kJ mol^{-1}), though not as strong as that in the N_2 molecule. Breaking this bond is therefore quite difficult, so the high activation energy for reactions like the combustion of hydrocarbons prevents these compounds being spontaneously flammable at room temperature. However, the small size of the oxygen atom leads it to form strong bonds with elements like hydrogen and carbon (bond energies $\text{H}-\text{O}$ 463 and $\text{C}=\text{O}$ $\sim 740 \text{ kJ mol}^{-1}$), contributing to the exothermic combustion of hydrocarbon fuels. The high charge/radius ratio of the O^{2-} ion leads to high lattice energies of ionic oxides, a factor favouring their formation. At very high pressure (20 Gpa) solid oxygen (O_2) turns to the ϵ -phase, which is dark red in colour. This contains O_8 units, in which four O_2 molecules are associated together by weak chemical bonds.

OZONE (TRIOXYGEN, O_3)



Ozone is an allotrope of oxygen, which is less stable than O_2 . It is a strong oxidising agent and harmful to life. In contrast to linear CO_2 , ozone forms a bent molecule (1.3). The central oxygen has two more electrons than the carbon in CO_2 ; they have to be accommodated as a lone pair.

It is formed in the upper atmosphere when ultraviolet light generates oxygen atoms, which then react with O_2 and form an ozone molecule. The subsequent decomposition of ozone also absorbs ultraviolet light, so these reactions in the “ozone layer” 30 km above the earth filter out much harmful ultraviolet radiation from the sun. Research in the mid-1970s by Frank Sherwood Rowland and Mario Molina showed that breakdown of CFCs (chlorofluorocarbons used as refrigerants, solvents, and aerosol propellants) in the upper atmosphere led to reactive $Cl\cdot$ radicals, which destroyed ozone. Together with Paul J. Crutzen, they were awarded the 1995 Nobel Prize for Chemistry; their research led to the 1987 Montreal protocol phasing out CFCs so that the ozone layer could recover.

Ozone is also produced at ground level, especially in cities. Sunlight acts on mixtures of hydrocarbons and nitrogen oxides emitted from car exhausts to form peroxyacylnitrates (PANs; $RCOOONO_2$ with $R = \text{alkyl}$); these are the compounds which typically make your eyes water on a hot summer’s day in city streets. They react further forming ground-level ozone, which, unlike the “ozone layer” in the stratosphere, is a bad thing. Because it is a strong oxidising agent, ozone is especially damaging to the human respiratory system and also damages organic materials like rubber. It has a sharp, chlorine-like smell, detectable at the 0.01 ppm level. Ozone is formed by the action of electrical discharges upon O_2 molecules, and the smell of ozone can sometimes be detected near electrical equipment like photocopiers.

Ozone has its uses commercially as an alternative to chlorine to disinfect water supplies and to kill bacteria in hospital operating theatres. It is also a useful reagent in chemical synthesis.

CARBON DIOXIDE, CO_2



For its abundance in the atmosphere, carbon dioxide (1.4) punches above its weight. Because it absorbs strongly in the infrared region, carbon dioxide, along with water, methane, and ozone, is a greenhouse gas. If not for a “natural greenhouse effect” reducing the loss of long-wavelength IR heat by radiation, the earth’s surface temperature would be around -20°C , not exactly hospitable. During my lifetime, the concentration of CO_2 has moved from just over 0.030% to nearly 0.04%. Controversy lies in the extent to which currently elevated temperatures, “global warming”, are due to an “enhanced greenhouse effect” from increases in these atmospheric greenhouse gases caused by human activity. As well as in combustion of fossil fuels and other carbon-based materials, CO_2 is emitted by respiration in plants and animals and, conversely, is removed from air by photosynthesis in green plants. Of the world’s CO_2 emissions, 5% come from cement making because it is formed when calcium carbonate is decomposed.

Carbon dioxide is acidic, well demonstrated by dropping a piece of dry ice into a beaker or measuring cylinder of water containing an acid–base indicator.

Unlike the other gases in the atmosphere, CO_2 only exists as a liquid above 5.1 atm pressure. Thus, chilling CO_2 gas below -78°C produces solid carbon dioxide; conversely, when solid CO_2 (“dry ice”) warms up, it turns directly to a gas and sublimates. This property is put to good employment when dry ice is used to refrigerate frozen foods because the packaging is not wetted. Liquid carbon dioxide can be heard, if not seen, in some CO_2 -containing fire extinguishers used for electrical fires. This “supercritical” CO_2 is used industrially as a nontoxic covalent solvent—not least to extract caffeine from coffee.

Carbon dioxide is slightly soluble in water, and the solubility increases significantly with increasing pressure; its pleasantly sharp taste was one of Joseph Priestley’s many discoveries (1772). His invention of soda water was taken up by Jacob Scheweppe, who founded a commercial empire. Carbonation of drinks is also employed in beers and sparkling wines. More importantly, much carbon dioxide is dissolved in this planet’s oceans. Increasing levels of CO_2 in the environment have led to a slight decrease in the pH of seawater, and concern is felt about the effects of this ocean acidification upon coral reefs and shellfish.

The inability of carbon dioxide to support combustion in any but the hottest fires (e.g., burning magnesium) is put to good use in fire extinguishers. Levels of CO_2 much more than 5% in air are dangerous to health, and there are caves in France and Italy where high levels of dense CO_2 near the cave floor are alleged to be lethal to dogs. Disturbance of lake water leading to release of CO_2 (originating in volcanic activity) associated with two “killer lakes” in Cameroon is believed to have killed 37 people at Lake Monoun in 1984 and 1,700 more around Lake Nyos 2 years later.

NOBLE GASES

At a time when scientists were discovering a number of new gases, Henry Cavendish (1731–1810) made important contributions. The significance of one experiment was not understood at the time (1785). He removed the nitrogen from air by sparking it with an excess of oxygen, dissolving the NO_x in water, then removing the remaining oxygen with potassium sulfide. This left a small amount of gas—just under 1% of the original volume—that simply would not react with anything. At the time, this was inexplicable.

Much later, on 19 April 1894, Lord Rayleigh announced to the Royal Society that nitrogen obtained from the air had a slightly greater density than nitrogen prepared from a chemical reaction. In the audience was William Ramsay, who was prompted to carry out an experiment in which he repeatedly passed 23 litres of aerial nitrogen backward and forward over hot magnesium (which reacted with the nitrogen, forming Mg_3N_2) until he was left with 100 cm^3 of totally unreactive gas. This turned out to be monoatomic and to have an atomic weight of 39.9. He called it argon.

The following year, Ramsay examined the gas formed when the uranium-containing mineral cleveite reacted with sulfuric acid; removing nitrogen and oxygen, he was left with a gas whose spectrum contained the same absorption at 587.49 nm already

TABLE 1.1
Abundance of Gases in
the Earth's Atmosphere

Gas	%	ppm
N ₂	78.1	781,000
O ₂	20.9	209,000
CO ₂	0.0390	390
He	5.2×10^{-4}	5.2
Ne	1.82×10^{-3}	18.2
Ar	0.93	9,340
Kr	1.14×10^{-4}	1.14
Xe	8.6×10^{-6}	0.086
Rn	Variable	Variable

noted in the solar spectrum in 1865 by Lockyer and Janssen. Ramsay had thus isolated helium, and in 1898 he obtained neon, krypton, and xenon by fractional distillation of liquid air. Dorn identified radon in 1900.

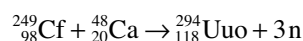
At that time, no one could explain why all these gases were made up of single atoms; it was 20 years before it was postulated that a filled outer shell of electrons was needed for stability. Chemists tried unsuccessfully to form compounds with them; thus, in 1895, Henri Moissan tried unsuccessfully to make an argon fluoride, but it was not until 1962 that Neil Bartlett made the first xenon compound. Compounds stable at room temperature are now known for Xe, Rn, and Kr. HArF is stable at -233°C .

Across the universe, the abundance of the noble gases decreases with increasing atomic number, as expected. Two factors modify this pattern on earth (Table 1.1); argon is by far the most abundant (0.93% of the atmosphere) because ^{40}Ar is generated by β -decay of ^{40}K in rocks. Helium is only the third most abundant noble gas; despite being generated by α -decay of U and Th minerals, it is too light to be retained by the earth's gravity (as with H₂). The abundance of radon varies, depending on the levels of radon-emitting minerals in a region, but in some regions it represents a very real cause of cancer. The recent (2011) isolation of XeO₂ adds to speculation that insertion of Xe into SiO₂ in the earth's crust may lead to atmospheric xenon depletion.

Despite their lack of reactivity, the noble gases have several uses. Because it has the lowest boiling point of any substance, liquid helium (b.p. 4.2K) is a vital coolant, especially for superconducting magnets (e.g., in magnetic resonance imaging spectrometers). On account of its low density and lack of flammability, it replaced hydrogen as a lifting gas for airships. Helium has a very low solubility in water (or blood) and is used in He–O₂ breathing mixtures in place of nitrogen because it eliminates the “bends”.

Several noble gases give a coloured glow when an electric current is passed through them; they are used in advertising lighting—classically, in red “neon signs”.

Xenon lamps are used in car headlights. Argon is used as a filler gas for traditional (filament-type) incandescent light bulbs, as well as in providing inert atmospheres when welding reactive metals. Element 118 (ununoctium), the seventh member of this group, was synthesised by Russian and American researchers led by Yuri Oganessian and reported in 2006. They used nuclear reactions such as



The atoms have lifetimes in the order of a millisecond, so chemical study is not feasible. Predictions suggest that this element would have a boiling point ca. 80°C; if so, it would not be an “inert” gas.

WATER



Over 70% of the surface of the earth is covered in water; the vast majority of it (97%) is in the oceans. We in the Western world are inclined to take it for granted, never having had to walk miles to get drinking water because we have chlorinated water on tap. It is quite conceivable that water supply may yet become a major international issue.

Water in itself is a remarkable substance. It is nontoxic; its boiling point of 100°C is much greater than that of other molecules of the same size, like methane (−162°C) or even ammonia (−33°C); and its liquid range coincides with ambient temperatures on much of the earth. Without these properties, human life on the planet would not be possible. Its solvent properties are also vital; its polar nature enables solvation of ions, whilst it can hydrogen-bond to many covalent molecules. It transports substances through organisms. Water vapour in the atmosphere contributes to the natural greenhouse effect, ensuring a steady ambient temperature conducive to the maintenance of life.

Because the electronegativity of oxygen is much greater than that of hydrogen, the water molecule is polar. Electron density in the O–H bond is strongly polarised toward oxygen, leaving the hydrogen with a very slight positive charge. The attraction between such a hydrogen and a lone pair of electrons belonging to another water molecule constitutes a significant intermolecular force: a hydrogen bond (Figure 1.1). This can also occur with molecules containing N–H and H–F bonds (but not C–H). The fact that a water molecule has two polar O–H bonds and two lone pairs means that it can participate in up to four hydrogen bonds to neighbouring molecules, an *optimum* number compared to NH₃ or HF, which therefore have weaker intermolecular forces and lower boiling points.

In fact, the number of hydrogen bonds per water molecule is slightly greater in ice than in liquid water, leading to a more open structure, a lower density for the solid form, and hence the unusual property of ice floating on water or ice expanding out of the ice-cube maker tray in the freezer compartment of the ‘fridge. The strength

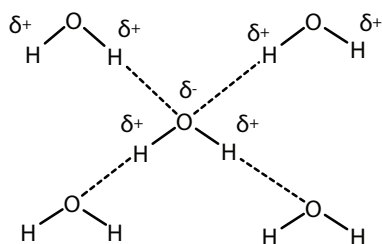


FIGURE 1.1 Hydrogen bond.

of hydrogen bonding also leads to the high surface tension of water, enabling pond skaters and needles to float on it, and to its capillary action (so that it can reach the top of high trees). Another anomalous property of water is that its greatest density occurs at 3.98°C, so in winter there is almost always liquid water at the bottom of lakes, enabling fish to survive.

In the late 1960s, scientists in the West became aware of experiments conducted by Boris Derjaguin in which water condensed in capillary tubes was found to have an anomalously high boiling point and density. Its infrared spectrum was different from that of ordinary water, and it was suggested that water molecules were associated in clusters. The word “polywater” was coined, and something of a media-fed frenzy began, with suggestions that this material was dangerous. It was subsequently discovered that this “polywater” contained hydrated silica and salts leached out of the glass or quartz tubes, but not before over 500 scientific papers had been published and some scientific reputations tarnished.

DEUTERIUM OXIDE (HEAVY WATER)

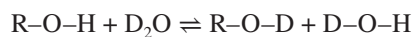


(1.6)

For most practical purposes, substituting one isotope for another in a compound has no effect on bulk physical properties. In the case of such a light molecule as water, the difference between H_2O and D_2O leads to significantly different melting points (0°C and 3.81°C, respectively) and boiling points (100°C and 101.42°C, respectively); G. N. Lewis and his student, Ronald T. MacDonald, were therefore able to obtain pure deuterium oxide (1.6) by fractional distillation under reduced pressure in 1933. Molecular dimensions of the isolated molecules are very slightly different; for an isolated H_2O molecule, O–H is 0.9724 Å and H–O–H is 104.50°, whilst for an isolated D_2O molecule, O–D is 0.9687 Å and D–O–D is 104.35°. In the condensed liquid phase, the O–H bond in H_2O is 1.01 Å, whilst the O–D bond in D_2O is 0.98 Å, shorter by 0.03 Å; on the other hand, the intermolecular bond in D_2O is longer by 0.07 Å.

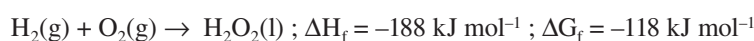
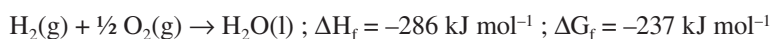
One significant difference between H_2O and D_2O is that deuterium oxide can act as a moderator in a nuclear reactor to produce neutrons of the right velocity to induce nuclear fission in ^{235}U . In the late 1930s and in the early years of World War II, this

led to competition between the Germans and French for supplies of heavy water and, subsequently, to attacks on the Ryukan plant in Norway that produced it; the film *Heroes of Telemark*, starring Kirk Douglas and Richard Harris, was loosely based upon these events. Since the war, chemists have made use of the different nuclear properties of hydrogen and deuterium in a different way; a compound with labile N–H or O–H groups will exchange the hydrogens on shaking with heavy water, so the signal due to these hydrogens in the proton nuclear magnetic resonance spectrum of the compound will disappear, facilitating assignment of the spectrum.



HYDROGEN PEROXIDE

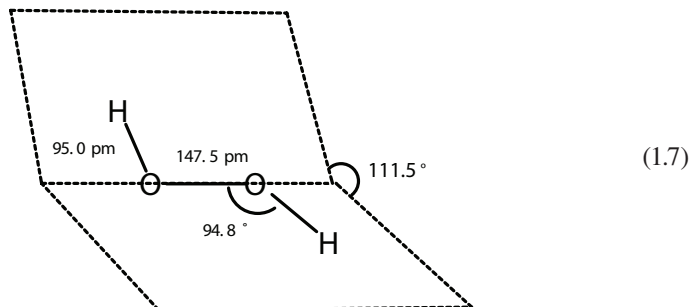
Hydrogen and oxygen form one more binary compound, H_2O_2 . Like water, hydrogen peroxide (1.7) is stable with respect to the elements:



But hydrogen peroxide is thermodynamically unstable with respect to decomposition to water and oxygen:



The activation energy for this decomposition is fairly high at 75 kJ mol^{-1} , but is greatly lowered by catalysts such as dust, MnO_2 ($E_{\text{a}} = 58 \text{ kJ mol}^{-1}$), and, particularly, the enzyme catalase ($E_{\text{a}} = 23 \text{ kJ mol}^{-1}$). Thus, solutions of H_2O_2 are normally kept in polythene or Teflon bottles and stabilisers added.



Hydrogen peroxide has an unusual skewed structure with a dihedral angle of 111.5° (gas phase), which minimises repulsion between the lone pairs and the O–H bond pairs. The dihedral angle is affected by hydrogen bonding; it is 90.2° in solid H_2O_2 .

Small amounts of H_2O_2 exist in our bodies as by-products of cellular respiration in cells. This could be very damaging to the cells, were it not for the presence of very

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